

# SCIENCE FOR GLASS PRODUCTION

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## VIBRATIONAL SPECTROSCOPY INVESTIGATION OF THE STRUCTURE OF MULTICOMPONENT PHOSPHORUS-CONTAINING SILICATE GLASSES

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IR spectroscopy and Raman scattering have been used to study the structure of multicomponent silicate glass with phosphorus oxide addition, simulating the commercial compositions of container glass and sheet float-glass. It is established that  $P_2O_5$  addition gives a micro-nonuniform structure consisting of silicon oxide anionic groupings, with different degrees of connectedness, and orthophosphate groupings. Such nonuniformity promotes subsequent liquation and crystallization of multicomponent glasses containing phosphorus.

**Key words:** silicate glasses, phosphorus additives, structure, vibrational spectroscopy

The influence of phosphorus oxide addition on the structure and properties of silicate melts and glasses has never been adequately studied. But, as noted in [1], this influence can be considerable even for low phosphorus concentrations. It must be taken into account when phosphorus oxide addition is used to obtain opacified glasses and glazes as well as to improve the process characteristics of glass-forming melts.

It is shown in [2, 3] that small phosphorus oxide addition (0.3–1.0 wt.%) has a positive effect on the process characteristics of commercial mass-produced silicate glass. Specifically, the liquidus temperature decreases, the glass making temperature can decrease, and the glass can be made less expensive by decreasing its content of alkali oxides and increasing its content of calcium oxide.

There are only a few works investigating the structure of multicomponent silicate glasses with phosphorus oxide addition, and they do not give a complete picture of the structural position of phosphorus in the silica matrix. The density, microhardness, and dilatometric indicators are sensitive to phosphorus-induced structural changes [4].

In the present article we present the results of our study, using vibrational spectroscopy, of the structure of multicomponent glasses with  $P_2O_5$  additions. Experimental T-series glass simulating commercial container glass and containing

no magnesium oxide and L-series glass simulating sheet float-glass were investigated.

Phosphorus oxide was introduced into the glass in the amounts 0.3–3.0% (molar content) as a replacement for  $SiO_2$ . Sodium hydrophosphate was used to introduce  $P_2O_5$ . The method described in [4] was used to synthesize, make, and anneal the glass. The chemical composition of the glass obtained (by synthesis) and the results of a complete chemical analysis of some samples are presented in Table 1.

The main problem of our investigation was to study the influence of small phosphorus oxide addition (doping) on the structure of synthesized glass. The structure was studied using Raman scattering and IR spectroscopy.

The Raman spectra were recorded on an experimental facility based on a MFS-24 dual monochromator. A LTI-701 pulsed solid state laser (wavelength 532 nm, pulse power 1 W), operating at modulation frequency 8.7 kHz with pulse duration 2  $\mu$ sec on an acousto-optic shutter, was used as the source to excite the spectra. The spectral width of the slit was  $7\text{ cm}^{-1}$  in all experiments. A VERTEX 70 IR Fourier spectrometer was used to measure the infrared spectra in the wavenumber range  $370\text{--}7500\text{ cm}^{-1}$ . The experimental samples were prepared by pressing powder consisting of glass and KBr into pellets.

The Raman spectra of the experimental glasses are presented in Fig. 1. Comparing the series T and L model glasses shows that these glasses are qualitatively similar, indicating that even though their composition is not quite the same they resemble one another structurally.

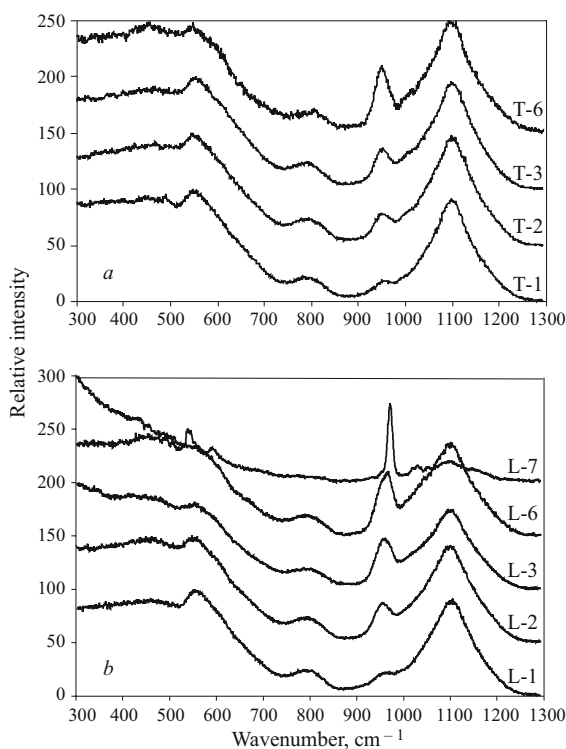
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TABLE 1.

Model glass	Content, %													
	SiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		CaO		MgO		Na <sub>2</sub> O		P <sub>2</sub> O <sub>5</sub>		Fe <sub>2</sub> O <sub>3</sub> <sup>*</sup> (mass)	K <sub>2</sub> O <sup>*</sup> (mass)
	molar	mass	molar	mass	molar	mass	molar	mass	molar	mass	molar	mass		
T-1	74.0	73.40	1.5	2.53	10.5	9.72	—	—	14.0	14.35	—	—	—	—
		73.97*		2.33*		8.70*				14.70*	—	—	0.05	0.25
T-2	73.7	72.81	1.5	2.52	10.5	9.68	—	—	14.0	14.29	0.3	0.70	—	—
		73.56*		2.23*		9.19*				14.02*		0.70*	0.05	0.25
T-3	73.4	72.22	1.5	2.51	10.5	9.64	—	—	14.0	14.23	0.6	1.40	—	—
T-4	73.1	71.63	1.5	2.50	10.5	9.60	—	—	14.0	14.18	0.9	2.09	—	—
T-6	72.5	70.48	1.5	2.48	10.5	9.53	—	—	14.0	14.06	1.5	3.45	—	—
L-1	71.0	72.06	1.0	1.73	9.0	8.53	6.0	4.06	13.0	13.63	—	—	—	—
		74.38*		2.18*		6.22*		3.35*		13.82*			0.06	
L-2	70.7	71.46	1.0	1.72	9.0	8.49	6.0	4.04	13.0	13.58	0.3	0.72	—	—
L-3	70.4	70.86	1.0	1.71	9.0	8.45	6.0	4.03	13.0	13.52	0.6	1.43	—	—
L-5	69.8	69.68	1.0	1.70	9.0	8.39	6.0	3.99	13.0	13.41	1.2	2.84	—	—
L-6	69.5	69.10	1.0	1.69	9.0	8.35	6.0	3.98	13.0	13.36	1.5	3.53	—	—
L-7	68.0	66.26	1.0	1.66	9.0	8.18	6.0	3.90	13.0	13.09	3.0	6.92	—	—
		66.90*		2.46*		5.76*		3.03*		15.03*		6.83*		

\* The chemical analysis of the glasses was performed in the Central Plant Laboratory of “Irbis Glass Works” JSC.



**Fig. 1.** Raman spectra of the T (a) and L (b) series model glasses. The labels on the spectra follow the composition number in Table 1.

A wide band peaking at  $1100\text{ cm}^{-1}$  is present in the spectra of all glasses except the glass L-7. This band is also present in the spectra of the T-1 and L-1 samples which do

not contain  $\text{P}_2\text{O}_5$ ; it is due to the vibrations of the non-bridge Si – O<sup>-</sup> bonds in the structural units  $Q^3$  which are fragments of the silicon – oxygen sheet structures and are tetrahedra  $[\text{SiO}_4]$  with three bridge oxygen atoms and one non-bridge oxygen atom [1, 5]. In addition, a weak band near  $950\text{ cm}^{-1}$  is present in the T-1 and L-1 spectra; this band is due to the presence of a small quantity of relatively de-polymerized structural units  $Q^2$  with two non-bridge oxygen atoms. The band peaking at  $800\text{ cm}^{-1}$  is due to deformation vibrations of Si – O – Si bands in the glass in microregions whose structure is close to that of the glassy  $\text{SiO}_2$  and consists of  $Q^4$  units. These completely polymerized units with all bridge bonds have no characteristic bands in the high-frequency region of the Raman spectra. The wide band near  $540 - 560\text{ cm}^{-1}$  is due to symmetric stretching and, in part, deformation vibrations of Si – O – Si bridges. On the whole the T-1 and L-1 Raman spectra are typical for the spectra of simple alkali and alkali-earth high-silica glasses.

When phosphorus oxide is introduced the intensity of the  $950\text{ cm}^{-1}$  band increases, and the intensity increases with the  $\text{P}_2\text{O}_5$  concentration in the glasses. However, this is not due to the de-polymerization of the silicon-oxygen network of the glass and, correspondingly, increasing content of the structural units  $Q^2$ , i.e., phosphorus oxide is not a modifying oxide. We believe that this is due to the superposition on the characteristic band of the structural units  $Q^2$  of a new band which can be attributed to symmetric stretching vibrations of non-bridge oxygen atoms in orthophosphate tetrahedra  $[\text{PO}_4^{3-}]$  [6 – 8]. This is confirmed by the spectra of the sample L-7, where a narrow band at  $960\text{ cm}^{-1}$  dominates; this

band is characteristic of, for example, apatite containing the grouping  $\text{PO}_4^{3-}$ , and the appearance of this band indicates crystallization of calcium orthophosphate in the glass. The structural investigation of the L-7 sample performed with an electron microscope (replica method and in transmission) showed the presence of liquation, and x-ray phase analysis showed crystallization — the formation of calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  and  $\beta$ -cristobalite ( $\text{SiO}_2$ ).

Analysis of the IR transmission spectra (Fig. 2) shows the presence of a weak band at  $3450\text{ cm}^{-1}$  due to vibrations of hydroxyl groups  $\text{OH}^-$  as well as intense bands at  $1065$  and  $470\text{ cm}^{-1}$  due to, respectively, asymmetric stretching and deformation vibrations of  $\text{Si}-\text{O}-\text{Si}$  bonds in the spectra of glasses in both series with no  $\text{P}_2\text{O}_5$  (L-1 and T-1) [9]. The band at  $785\text{ cm}^{-1}$  is due to the vibrations of  $\text{Al}-\text{O}$  bonds in  $[\text{AlO}_4^-]$  tetrahedra. Small  $\text{P}_2\text{O}_5$  additions (L-2 and T-2 samples with 0.3%  $\text{P}_2\text{O}_5$ ) do not change the IR spectra. But at the same time a new absorption band appears at  $575\text{ cm}^{-1}$  in the spectrum of T-3 glass with 0.6%  $\text{P}_2\text{O}_5$ ; this band is due to deformation vibrations of  $\text{O}-\text{P}-\text{O}$  bonds in orthophosphate groupings  $\text{PO}_4^{3-}$  [10]. For the partially de-crystallized sample L-7 this band is much stronger and another (weak) band is observed at  $600\text{ cm}^{-1}$ . This agrees well with the fact that two bands peaking at  $576$  and  $605\text{ cm}^{-1}$  are recorded in the IR spectra of anatite in the region of deformation vibrations [11].

In summary, vibrational spectroscopy investigations shows that  $\text{P}_2\text{O}_5$  addition in silicate glasses results in the formation of micro-nonuniform structure, containing as one component highly polymerized silicon-oxygen anionic groupings constructed from the structural units  $Q^3$  and  $Q^4$ , while the phosphate part is represented by the maximally de-polymerized orthophosphate groupings  $\text{PO}_4^{3-}$ . Such a micro-nonuniform structure promotes subsequent liquation and crystallization of multicomponent silicate glasses containing phosphorus.

## REFERENCES

1. V. N. Anfilov, V. N. Bykov, and A. A. Osipov, *Silicate Melts* [in Russian], Nauka, Moscow (2005).
2. B. G. Varshal and E. I. Raevskaya, "Sheet glass with phosphorus pentoxide additives," *Steklo Keram.*, No. 5, 10 – 13 (1990).
3. P. A. Bingham, "The effects of 1 wt.%  $\text{P}_2\text{O}_5$  addition on the properties of container glass," *Glass Technol.*, No. 6, 255 – 228 (2004).
4. S. V. Mulevanov, N. I. Min'ko, and S. A. Kemenov, "Effect of phosphorus oxide on the dilatometric properties of container silicate glass," *Steklo Keram.*, No. 11, 17 – 20 (2007).
5. P. McMillan, "Structural studies of silicate glasses and melts: application and limitation of Raman spectroscopy," *Am. Miner.*, **69**(7/8), 622 – 644 (1984).
6. A. L. Lazarev, *Vibrational Spectra and Structure of Silicates* [in Russian], Nauka, Leningrad (1968).
7. R. K. Brow, "Review: the structure of simple phosphate glasses," *J. Non-Cryst. Solids*, **263** – **264**, 1 – 28 (2000).
8. A. V. Baranov, V. V. Golubkov, and V. I. Petrov, "Investigation of the structure of pyrophosphate glasses by Raman and x-ray low-angle scattering," *Fiz. Khim. Stekla*, **25**(4), 385 – 401 (1999).
9. W. R. Taylor, "Application of infrared spectroscopy to studies of silicate glass structure: examples from the melilite glasses and the systems  $\text{Na}_2\text{O}-\text{SiO}_2$  and  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ," *Proc. Indian Academy of Sciences. Earth and Planetary Sciences*, **99**, 99 – 117 (1990).
10. K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York (2009).
11. V. F. Barabanov (ed.), *Modern Physical Methods in Geochemistry* [in Russian], Izd. Leningrad. Univer., Leningrad (1990).

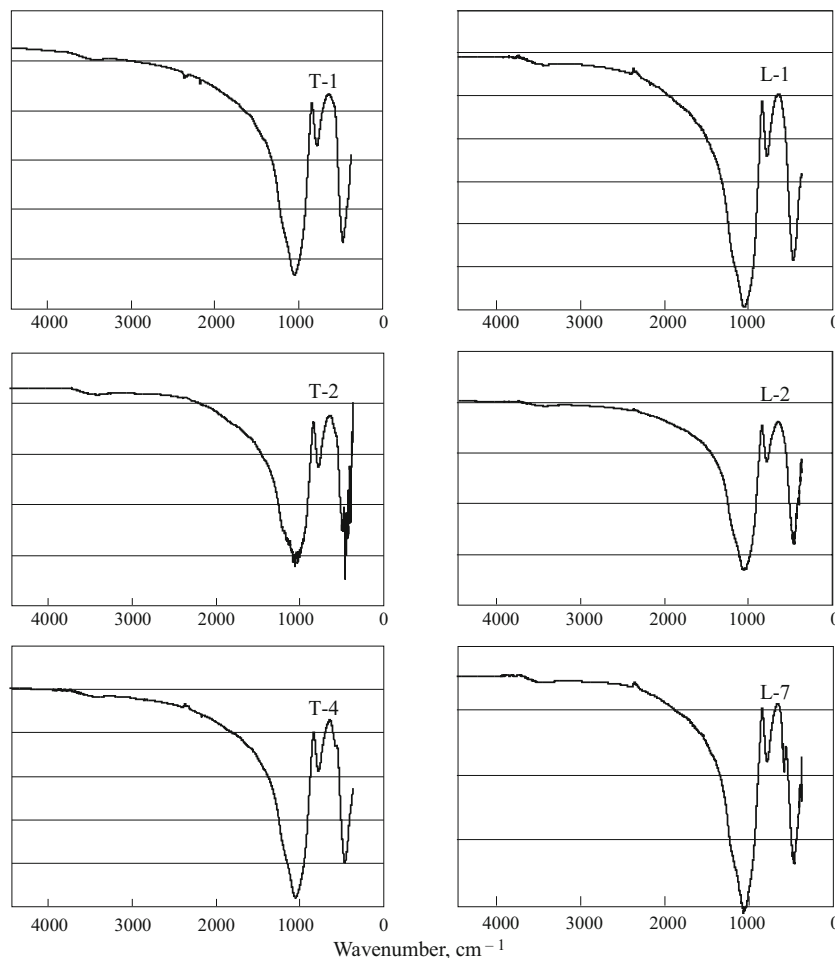


Fig. 2. IR transmission spectra of T and L series model glasses.